CLAIMS

1. A fluoropolymer solid composition which contains a fine particle comprising a fluoropolymer,

said fluoropolymer having an acid/acid salt group,

said acid/acid salt group being a sulfonic acid group, $-SO_2NR^{17}R^{18}$, a carboxyl group, $-SO_3NR^1R^2R^3R^4$, $-SO_3M^1{}_{1/L}$, $-COONR^5R^6R^7R^8$ or $-COOM^2{}_{1/L}$ (in which R^{17} and R^{18} are the same or different and each represents a hydrogen atom, an alkali metal, an alkyl group or a sulfonyl-containing group, R^1, R^2, R^3 and R^4 are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R^5, R^6, R^7 and R^8 are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, M^1 and M^2 are the same or different and each represents a metal whose valence is L, and said metal whose valence is L is a metal belonging to the group 1, 2, 4, 8, 11, 12 or 13 of the periodic table);

said fine particle comprising the fluoropolymer containing, at the proportion of at least 25% by mass thereof, a spherical fluoropolymer fine particle, and

said spherical fluoropolymer fine particle being substantially spherical.

2. The fluoropolymer solid composition according to Claim 1,

wherein the fine particle comprising the fluoropolymer contains the spherical fluoropolymer fine particle at the proportion of at least 50% by mass thereof.

3. The fluoropolymer solid composition according to Claim 1 or 2,

wherein the spherical fluoropolymer fine particle has an average particle diameter of not smaller than 10 nm.

4. The fluoropolymer solid composition according to Claim

1 or 2,

wherein the spherical fluoropolymer fine particle has an average particle diameter of 10 to 300 nm.

5. The fluoropolymer solid composition according to Claim 1 or 2,

wherein the spherical fluoropolymer fine particle has an average particle diameter of 30 to 160 nm.

6. The fluoropolymer solid composition according to Claim 1, 2, 3, 4 or 5,

wherein an existence of the acid/acid salt groups on a particle surface of the fine particles comprising fluoropolymers is more than that in the particle inside thereof.

7. The fluoropolymer solid composition according to Claim 1, 2, 3, 4, 5 or 6,

wherein the acid/acid salt group is bound to a fluoroether side chain represented by the following general formula (I):

$$-O-(CF_2CFY^1-O)_n-(CFY^2)_m- \qquad (I)$$

in which Y^1 represents a fluorine atom, a chlorine atom or a perfluoroalkyl group; n represents an integer of 0 to 3, and n atoms/groups of Y^1 may be the same or different; Y^2 represents a fluorine atom or a chlorine atom; m represents an integer of 1 to 5, and m atoms of Y^2 may be the same or different,

said fluoroether side chain being bound, in the manner of ether bonding, to a carbon atom constituting a perfluoroethylene unit in a main chain of the fluoropolymer.

8. A fluoropolymer dispersion

which comprises the fluoropolymer solid composition according to Claim 1, 2, 3, 4, 5, 6 or 7 as dispersed in a liquid medium.

9. The fluoropolymer dispersion according to Claim 8,

wherein the fluoropolymer solid composition amounts to 2 to 80% by mass based on the total mass of the fluoropolymer dispersion.

10. The fluoropolymer dispersion according to Claim 8 or 9,

wherein the liquid medium is an aqueous dispersion medium,

said aqueous dispersion medium having a water content of 10 to 100% by mass.

11. A method for producing a fluoropolymer dispersion to give the fluoropolymer dispersion where a fine particle comprising a fluoropolymer is dispersed in an aqueous dispersion medium,

said fluoropolymer having a sulfonic acid group and/or carboxyl group, and

said method comprising a hydrolysis step of hydrolyzing, in an aqueous medium, $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms) which a fluoropolymer precursor has thereby to give the fluoropolymer.

12. The method for producing a fluoropolymer dispersion according to Claim 11,

wherein the sulfonic acid group and/or carboxyl group each is bound to a fluoroether side chain represented by the following general formula (I):

$$-O-(CF_2CFY^1-O)_n-(CFY^2)_m- \qquad (I)$$

wherein Y^1 represents a fluorine atom, a chlorine atom or a perfluoroalkyl group; n represents an integer of 0 to 3, and n atoms/groups of Y^1 may be the same or different; Y^2 represents a fluorine atom or a chlorine atom; m represents an integer of 1 to 5, and m atoms of Y^2 may be the same or different, and

wherein said fluoroether side chain is bound, in the manner

of ether bonding, to a carbon atom constituting a perfluoroethylene unit in a main chain of the fluoropolymer.

13. The method for producing a fluoropolymer dispersion according to Claim 11 or 12,

wherein the aqueous medium is one originating from an aqueous reaction medium in a polymerization reaction,

said polymerization reaction giving the fluoropolymer precursor.

14. The method for producing a fluoropolymer dispersion according to Claim 13,

wherein the polymerization reaction is carried out by emulsion polymerization.

15. The method for producing a fluoropolymer dispersion according to Claim 11, 12, 13 or 14,

wherein the aqueous dispersion medium in the fluoropolymer dispersion is one originating from the aqueous medium.

16. The method for producing a fluoropolymer dispersion according to Claim 11, 12, 13, 14 or 15,

wherein the fluoropolymer precursor is one obtainable by polymerizing a fluorovinyl ether derivative represented by the following general formula (II):

$$CF_2=CF-O-(CF_2CFY^1-O)_n-(CFY^2)_m-A^1 \qquad (II)$$

wherein Y^1 represents a fluorine atom, a chlorine atom or a perfluoroalkyl group; n represents an integer of 0 to 3, and n atoms/groups of Y^1 may be the same or different; Y^2 represents a fluorine atom or a chlorine atom; m represents an integer of 1 to 5, and m atoms of Y^2 may be the same or different; A^1 represents $-SO_2X$ or $-COZ^1$; X represents a halogen atom, $-OM^3$ or $-OM^4_{1/2}$, M^3 represents an alkali metal or $NR^9R^{10}R^{11}R^{12}$, M^4 represents an alkaline earth metal, R^9, R^{10}, R^{11} and R^{12} are the

same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and Z^1 represents an alkoxyl group having 1 to 4 carbon atoms).

17. The method for producing a fluoropolymer dispersion according to Claim 16,

wherein the fluoropolymer precursor is a binary or multinary copolymer obtainable by polymerizing the fluorovinyl ether derivative and a fluorine-containing ethylenic monomer.

18. The method for producing a fluoropolymer dispersion according to Claim 12, 16 or 17,

wherein Y^1 is a trifluoromethyl group, Y^2 is a fluorine atom, n is 0 or 1 and m is 2.

19. The method for producing a fluoropolymer dispersion according to Claim 11, 12, 13, 14, 15, 16, 17 or 18

which further comprises a polymerization reaction step of carrying out a polymerization reaction,

said polymerization reaction providing the fluoropolymer precursor,

said fluoropolymer dispersion being produced in an aqueous system through the polymerization reaction step and hydrolysis step, and

said fluoropolymer dispersion being produced without drying said fluoropolymer precursor and the fluoropolymer.

20. The method for producing a fluoropolymer dispersion according to Claim 19,

wherein the polymerization reaction is carried out by iodine transfer polymerization.

21. The method for producing a fluoropolymer dispersion according to Claim 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20,

wherein the hydrolysis step comprises hydrolysis and

neutralization respectively using with an alkali and an acid in that order,

wherein said fluoropolymer precursor has $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms).

22. The method for producing a fluoropolymer dispersion according to Claim 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20,

wherein the hydrolysis step comprises an alkali treatment step of treating a fluoropolymer precursor (P) with an alkali

and wherein said fluoropolymer precursor (P) has $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms).

23. The method for producing a fluoropolymer dispersion according to Claim 22,

wherein the hydrolysis step comprises an alkali treatment step and thereafter, a subsequent step of neutralization treatment with an acid.

24. The method for producing a fluoropolymer dispersion according to Claim 22 or 23,

wherein the hydrolysis step further comprises a step of removing a low-molecular-weight substance following the alkali treatment step, and

said low-molecular-weight substance being a residual monomer remaining in the polymerization reaction step, a polymerization initiator residue, an unrequired low-molecular-weight polymer, and/or a substance formed upon treatment of the fluoropolymer precursor (P) with an alkali.

25. The method for producing a fluoropolymer dispersion according to Claim 24,

wherein the step of removing a low-molecular-weight substance is carried out by ultrafiltration technique.

26. The method for producing a fluoropolymer dispersion according to Claim 22, 23, 24 or 25,

wherein the fluoropolymer precursor (P) has $-SO_2X^1$.

27. The method for producing a fluoropolymer dispersion according to Claim 19, 20 or 21,

wherein the hydrolysis step comprises the polymerization reaction step of obtaining the fluoropolymer precursor by polymerizing in the presence of a fluoromonomer (Pm) and a fluoromonomer (Qm), an alkali treatment step of treatment with an alkali and a step of neutralization treatment with an acid, in that order,

said fluoromonomer (Pm) having $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms), and

said fluoromonomer (Qm) having $-SO_2X^2$ (X^2 representing $-OM^3$ or $-OM^4_{1/2}$ in which M^3 represents an alkali metal or $NR^9R^{10}R^{11}R^{12}$ (in which R^9, R^{10}, R^{11} and R^{12} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms); and M^4 represents an alkaline earth metal) and/or $-COOZ^2$ (Z^2 representing M^5 or $M^6_{1/2}$ in which M^5 represents an alkali metal or $NR^{13}R^{14}R^{15}R^{16}$ (in which R^{13}, R^{14}, R^{15} and R^{16} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms); M^6 represents an alkaline earth metal).

28. The method for producing a fluoropolymer dispersion according to Claim 19, 20 or 21,

wherein the hydrolysis step comprises the polymerization reaction step of obtaining the fluoropolymer precursor by polymerizing in the presence of a fluoromonomer (Qm)-based polymer and a fluoromonomer (Pm), an alkali treatment step of treatment with an alkali and a step of neutralization treatment with an acid, in that order,

said fluoromonomer (Pm) having $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms), and

said fluoromonomer (Qm) having $-SO_2X^2$ (X^2 representing $-OM^3$ or $-OM^4_{1/2}$ in which M^3 represents an alkali metal or $NR^9R^{10}R^{11}R^{12}$ (in which R^9, R^{10}, R^{11} and R^{12} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms); and M^4 represents an alkaline earth metal) and/or $-COOZ^2$ (Z^2 representing M^5 or $M^6_{1/2}$ in which M^5 represents an alkali metal or $NR^{13}R^{14}R^{15}R^{16}$ (in which R^{13}, R^{14}, R^{15} and R^{16} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms); M^6 represents an alkaline earth metal).

29. The method for producing a fluoropolymer dispersion according to Claim 27 or 28,

wherein the hydrolysis step further comprises a step of removing a low-molecular-weight substance following the alkali treatment step,

said low-molecular-weight substance being a residual monomer remaining in the polymerization reaction step, a polymerization initiator residue, an unrequired low-molecular-weight polymer, and/or a substance formed upon treatment of the fluoropolymer precursor with an alkali.

30. The method for producing a fluoropolymer dispersion according to Claim 27, 28 or 29,

wherein the step of removing a low-molecular-weight substance is carried out by ultrafiltration technique.

31. The method for producing a fluoropolymer dispersion according to Claim 27, 28, 29 or 30,

wherein the fluoromonomer (Pm) has $-SO_2X^1$ and

wherein the fluoromonomer (Qm) has $-SO_2X^2$.

32. The method for producing a fluoropolymer dispersion according to Claim 27, 28, 29 or 30,

wherein the aqueous medium does not contain an emulsifier.

33. The method for producing a fluoropolymer dispersion according to Claim 32,

wherein the fluoropolymer precursor is one obtainable by carrying out the polymerization reaction in an emulsifier-free aqueous reaction medium.

34. A method for producing a fluoropolymer dispersion to give the fluoropolymer dispersion where a fine particle comprising a fluoropolymer is dispersed in a liquid medium,

said fluoropolymer having an acid salt group,

said acid salt group being $-SO_3NR^1R^2R^3R^4$, $-SO_3M^1{}_{1/L}$, $-COONR^5R^6R^7R^8$ or $-COOM^2{}_{1/L}$ (in which R^1, R^2, R^3 and R^4 are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R^5, R^6, R^7 and R^8 are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, M^1 and M^2 are the same or different and each represents a metal whose valence is L, and the metal whose valence is L is a metal belonging to the group 1, 2, 4, 8, 11, 12 or 13 of the periodic table), and

said method comprising a step of hydrolyzing, in an aqueous medium, $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms) which the fluoropolymer precursor has thereby to give the fluoropolymer.

35. The method for producing a fluoropolymer dispersion according to Claim 34,

wherein the hydrolysis step comprises a polymerization reaction step for obtaining a fluoropolymer precursor by carrying out a polymerization in the presence of a fluoromonomer

(Pm) and a fluoromonomer (Qm) and an alkali treatment step of treating with an alkali,

said fluoromonomer (Pm) having $-SO_2X^1$ (X^1 representing a halogen atom) and/or $-COZ^1$ (Z^1 representing an alkoxyl group having 1 to 4 carbon atoms), and

said fluoromonomer (Qm) having $-SO_2X^2$ (X^2 representing $-ONR^9R^{10}R^{11}R^{12}$ or $-OM^1{}_{1/L}$ in which R^9, R^{10}, R^{11} and R^{12} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, M^1 represents a metal whose valence is L, and the metal whose valence is L is a metal belonging to the group 1, 2, 4, 8, 11, 12 or 13 of the periodic table) and/or $-COOZ^2$ (Z^2 representing $NR^{13}R^{14}R^{15}R^{16}$ or $M^2{}_{1/L}$ in which R^{13}, R^{14}, R^{15} and R^{16} are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, M^2 represents a metal whose valence is L, and the metal whose valence is L is a metal belonging to the group 1, 2, 4, 8, 11, 12 or 13 of the periodic table).

36. The method for producing a fluoropolymer dispersion according to Claim 34 or 35,

wherein the hydrolysis step further comprises a step of removing a low-molecular-weight substance following the alkali treatment step,

said low-molecular-weight substances being a residual monomer remaining in the polymerization reaction step, a polymerization initiator residue, an unrequired low-molecular-weight polymer, and/or a substance formed upon treatment of the fluoropolymer precursor with an alkali.

37. A fluoropolymer dispersion obtainable by the method for producing a fluoropolymer dispersion according to Claim 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35 or 36.

38. A dispersion composition for thin film formation

which comprises the fluoropolymer dispersion according to Claim 8, 9, 10 or 37 and at least one alcohol selected from the group consisting of methanol, ethanol, propanol and tetrafluoropropanol.

39. A film/membrane obtainable by cast film formation using the fluoropolymer dispersion according to Claim 8, 9, 10 or 37 or the dispersion composition for thin film formation according to Claim 38.

40. A film/membrane obtainable by impregnating a porous support with the fluoropolymer dispersion according to Claim 8, 9, 10 or 37 or the dispersion composition for thin film formation according to Claim 38, followed by removal of the liquid medium.

41. An active substance-immobilized material comprising a fluoropolymer and an active substance

which is obtainable by applying, to a substrate, a liquid composition comprising the active substance and the fluoropolymer dispersion according to Claim 8, 9, 10 or 37 or the dispersion composition for thin film formation according to Claim 38.

42. The active substance-immobilized material according to Claim 41,

wherein the active substance is a catalyst.

43. The active substance-immobilized material according to Claim 42,

wherein the catalyst is a metal comprising platinum.

44. An electrolyte membrane

comprising the active substance-immobilized material according to Claim 42 or 43.

45. A solid polymer electrolyte fuel cell comprising the electrolyte membrane according to Claim 44.

46. A method for producing an acid-derivative-type-group-containing fluorocopolymer which comprises carrying out a polymerization reaction of a fluorovinyl ether derivative (Rm) represented by the follwoing general formula (VI):

$$CF_2=CF-O-(CF_2CFY^1-O)_n-(CFY^2)_m-A^5 \qquad (VI)$$

(wherein Y^1 represents a fluorine atom, a chlorine atom or a perfluoroalkyl group; n represents an integer of 0 to 3, and n atoms/groups of Y^1 are the same or different; Y^2 represents a fluorine atom or a chlorine atom; m represents an integer of 1 to 5, and m atoms of Y^2 may be the same or different; A^5 represents $-SO_2X^1$, $-COZ^1$ and/or $-CONR^{19}R^{20}$; X^1 represents a halogen atom, Z^1 represents an alkoxyl group having 1 to 4 carbon atoms, and R^{19} and R^{20} are the same or different and each represents a hydrogen atom, an alkali metal, an alkyl group or a sulfonyl-containing group) in an aqueous reaction medium to thereby give the acid-derivative-type-group-containing fluorocopolymer,

said polymerization reaction being carried out with an acid/acid salt fluorovinyl ether derivative represented by the following general formula (VII):

$$CF_2=CF-O-(CF_2CFY^1-O)_n-(CFY^2)_m-A^6 \qquad (VII)$$

(wherein Y^1 represents a fluorine atom, a chlorine atom or a perfluoroalkyl group; n represents an integer of 0 to 3, and n atoms/groups of Y^1 may be the same or different; Y^2 represents a fluorine atom or a chlorine atom; m represents an integer of 1 to 5, and m atoms of Y^2 may be the same or different; A^6 represents $-SO_2X^3$, $-SO_2NR^{17}R^{18}$ and/or $-COOZ^3$; X^3 represents $-OM^5$ or $-OM^6_{1/2}$; M^5 represents an alkali metal or $NR^1R^2R^3R^4$ in which R^1, R^2, R^3 and R^4 are the same or different and each represents

a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; M^6 represents an alkaline earth metal; R^{17} and R^{18} are the same or different and each represents a hydrogen atom, an alkali metal, an alkyl group or a sulfonyl-containing group; Z^3 represents M^7 or $M^8_{1/2}$; M^7 represents an alkali metal or $NR^5R^6R^7R^8$ in which R^5, R^6, R^7 and R^8 are the same or different and each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and M^8 represents an alkaline earth metal).

47. The method for producing the acid-derivative-type-group-containing fluorocopolymer according to Claim 46,

wherein the polymerization reaction is carried out without using an existing emulsifiers.